square of the concentration. The very-low-temperature specific heat (0.4 to 1.5°K) of Cu-Fe comes from a region where $P(H_0)$ is independent of the concentration; hence C_v is approximately proportional to the concentration.

The calculated and experimental results for 0.2% Cu-Fe are compared in Fig. 1. On the same graph we show the results with the temperature-corrected correlation length given by Eq. (3). The calculated and experimental results for Cu-Co are shown in Fig. 2. We have plotted C_v/T vs the concentration on a logarithmic scale and find that for high temperatures and low concentrations the slope of the curve is 2, indicating a quadratic dependence of the concentration. For higher concentrations and lower temperatures, the slope of the curve becomes smaller, and at very low temperature becomes zero (not shown in Fig. 2). The agreement between theory and experiment is good for both substances. This agreement also holds for 0.05% and 0.1% Cu-Fe. The low-temperature specific-heat data on Cu-Fe indicate that JS^2 in iron is about 1.6 times that of manganese. With this value of JS^2 we show, in Fig. 3, the calculated values of $P(H)$ for 0.2% concentrated Cu-Fe for various temperatures. We note that the probability for having large fields increases with increasing temperatures. This is qualitatively in agreement with the reported results on Mössbauer experiments on Cu-Fe.[9] We also find that an 8% decrease in the correlation length makes the experimental and theoretical specific-heat curves shown in Fig. 1 practically coincide over the temperature range from 0 to 3°K.

We thank Dr. E. W. Prohofsky for many useful discussions.

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ORIGIN OF THE VISIBILITY OF THE ANTIPARALLEL 180° DOMAINS IN BARIUM TITANATE

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Miller and Savage[1] reported that the antiparallel 180° domain configuration in a *c* plate of the ferroelectric $BaTiO_3$ crystal was visible between crossed polaroids during polarization reversal. Their experiment is invaluable to the study of the polarization reversal in this crystal. But the origin of the effects which give rise to the visibility of antiparallel domains does not appear to have been resolved. Although domain switching characters have been extensively studied by many workers, it would be hardly too much to say that no research seems to have been directed to structural aspects of the domains in the process of their switching motion. The present communication describes new optical and x-ray evidence as to structure anomaly occurring in the sidewise growing domains. The evidence allows us to understand the origin of the visibility mentioned above.

Adopting the technique found by Miller and Savage,[2] we could also observe approximately square domains expanding sideways in a metal-electroded crystal as shown in Fig. 1(a). The salient visual character of these domains exists

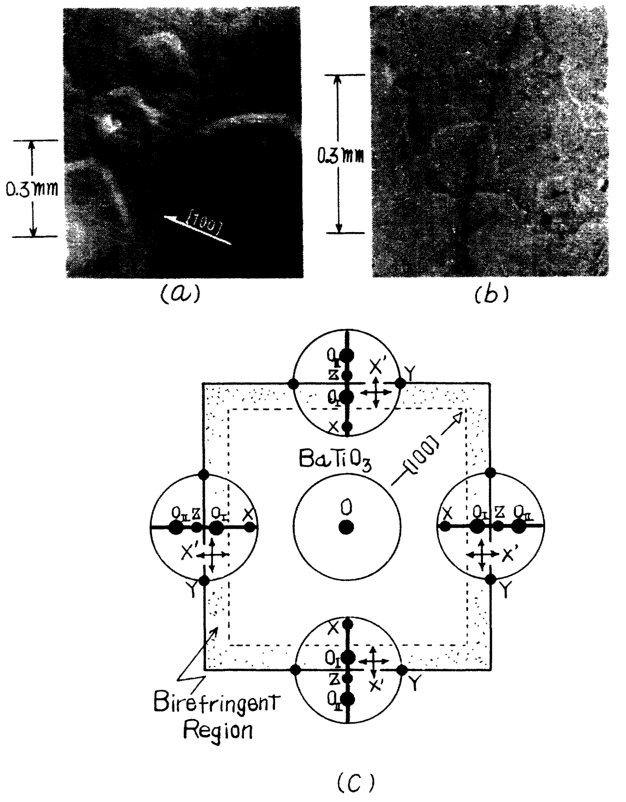

FIG. 1. Antiparallel domains in $BaTiO_3$. (a) Photomicrograph of antiparallel domains having clear dark and light contrast portions (*B* zones) as viewed with obliquely incident light; (b) antiparallel domains having uniformly dim contrast portions near the boundaries as viewed with normally incident light; (c) stereographic representation on (001) concerning the optical orientation of an approximately square domain (exaggerated): *O* denotes a unique optic axis of the tetragonal structure, $O_{\rm I}$ and $O_{\rm II}$ biaxial optic axes of the lower symmetry one. *X'* indicates the trace of the vibration plane of the fast component.

in the darker and lighter tones in portions near and parallel to domain walls than the surrounding region. Hereafter these portions are designated as *B* zones. Besides this feature the following points are outstanding: (1) Generally *B* zones become visible when domain walls are in sideways motion by an applied field; after removal of the field, their visibility disappears gradually. (2) The dark and the light positions in *B* zones of a domain are interchanged with a slight change of direction of the incident light. If direction of the incident light is adjusted so as to be closely perpendicular to the crystal plate, the *B* zones which were previously distinguished by the dark and light contrast are seen dim uniformly as shown in Fig. 1(b), the visibility necessarily becoming less conspicuous. So, the dark and light contrast appears only when any oblique illumination is used. (3) The dim *B* zones have definite extinction when the crystal is rotated between crossed polaroids. (4) Generally the contrast of a *B* zone depends on the sense of the procession of its related domain wall, irrespective of the sign of the polarization contained within the domain. For example, if *B* zones look dark when they move from the right to the left by an applied field, they do so when they move in the same direction by the reversed field. Our optical inspections (2) and (3) lead us to the conclusion that the *B* zones are no longer optically isotropic as viewed along the ferroelectric axis, but are slightly birefringent. That is to say, the contrast by which we could differentiate the antiparallel domains has turned out to be in its nature the interference colors due to the weak birefringence. The directions of vibrations of light in the *B* zones of a domain could be determined with a gypsum test plate. When a *B* zone parallel to one of the edges of square domain was brought into the 45° position, the interference color of this zone and of the other parallel zone on opposite side went up from the original red (sensitive tint of path difference $575\mu\mu$) to blue, while that of the other pair of zones went down to yellow. Therefore the trace of the vibration plane of the fast component was found normal to every domain boundary. Furthermore, as seen clearly in Fig. 1(a) the contrast of a pair of opposite *B* zones of a domain is always interchanged; this is nothing but a special case of (4) where two opposed walls move into opposite directions. This fact indicates that the optical orientation of a *B* zone is the mirror image of that of the opposed one. In Fig. 1(c) optical orientations of a square domain are shown by a stereographic projection on (001) plane, where *O* denotes a unique optic axis of the tetragonal crystal, while $O_{\rm I}$ and $O_{\rm II}$ biaxial ones of the *B* zones. The faster the domain wall moves, the larger the induced birefringence.

It is natural with the optical evidence to suspect that the crystal structure of the *B* zones changes from the original tetragonal into another lower symmetry, and recovers to the original one with a considerable relaxation time. By means of x-ray diffraction, we have disclosed this phenomenon actually to occur. If a crystal has such a domain as depicted in Fig. 1(c), its

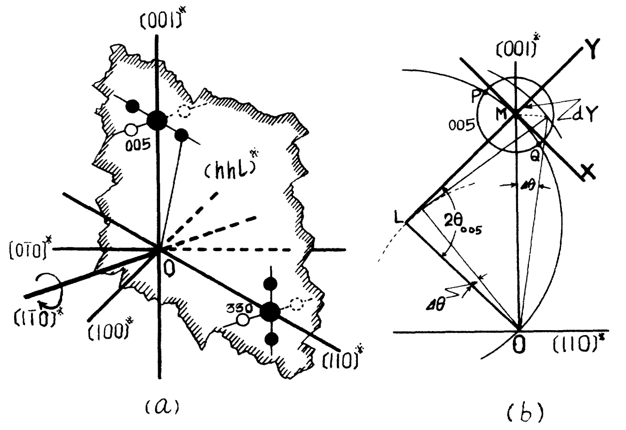

FIG. 2. Schematic illustration of the x-ray spectrometer experiment. (a) Hypothetical configuration of reciprocal lattice points in the neighborhood of 005 and 330 spectra in reciprocal lattice space of the specimen. Large circles correspond to the original tetragonal structure, small circles to lower symmetry structure. (b) Geometrical representation for the procedure of the diffraction intensity measurements, when particularly referred to 005 reflection. O denotes the origin of $(hhl)^*$ reciprocal lattice plane, L a center of the sphere of reflection, and M the reciprocal lattice point corresponding to 005 spectrum.

reciprocal lattice would be the composite of five lattices; the one corresponds to the original structure, the four others to lower symmetry structure. Therefore each original reciprocal lattice point (hhl) will be accompanied by four satellites, among which two are in a reciprocal $(hhl)^*$ plane as shown in Fig. 2(a) for 005 and 330 points. We tried to examine whether this configuration be realized in the neighborhood of 005 and 330 reciprocal lattice points by using an x-ray spectrometer, the crystal being rotated around its $[1\bar{1}0]$ axis. The radiation used was nonmonochromatized Cu K_α. During measurement of the diffraction intensities, the crystal was subjected to an alternating electric field by which domain switching was forced to occur repeatedly. The electric fields to reverse the polarization were given by periodic rectangular voltage pulses: one cycle consisting of 0.1-sec long 20-volt (corresponding to a field of 2 kV/cm) negative pulse (the eraser pulse), followed immediately by 0.1-sec long positive pulse (the forming pulse) of variable amplitude, and finally a 1.1-sec interval with no voltage. As the duration of no voltage is much longer than that of applied voltage in this pulse arrangement, the x-ray diffractions are regarded to be almost entirely due to the crystal having aftereffects of the domain reversal motions.

The geometrical illustration for the experimental procedure is shown in Fig. 2(b), where the sphere of reflection with radius LM (the radius being taken as unity) is drawn corresponding to the exact reflection of the reciprocal lattice point 005 in the reciprocal plane $(hhl)^*$ having its origin at O. For this direction of incidence LO, diffraction can take place in a variety of directions corresponding to intersection PMQ of the sphere of reflection with the intensity distribution around M. As the breadth of the intensity distribution is very small compared with the radius of the sphere of reflection, PMQ can be regarded to coincide with the tangent line MX in the immediate neighborhood of M. Let the line MX be defined as the X axis, and the other line normal to MX as the Y axis. Then a rotation of the crystal by $\Delta\theta$ from maximum reflection position corresponds to a parallel movement of the line PMQ to itself through a distance $dY = \sin 2\theta_{005}\Delta\theta$. Thus the Y axis denotes the orientation of the crystal, while the X axis denotes the direction of diffraction. In practice, the crystal was rotated from $\Delta\theta = -15'$ to $+15'$ at an interval of $1'$. At every Y setting the diffraction intensity was scanned by a GM counter through a receiving slit, which is 0.1 mm wide and 280 mm from the crystal. Observed intensity as a function of X at each run was plotted on a X-Y net in a reciprocal lattice $(hhl)^*$; thus the intensity distributions expressed as contour lines were produced.

Figure 3 shows some examples of the intensity distributions of 005 reflection under various conditions of applied field E; (a) corresponds to $E = 0$ kV/cm, (b) to $E = 7$ kV/cm, and (c) to $E = 19$ kV/cm. In each figure, X and Y axes are also drawn. We have inquired into the extent of broadening of the resultant intensity distributions due to external conditions such as temperature fluctuation of the crystal, the optical system, and the inhomogeneity of the radiation. The observed change of spacing Δd_{005} was so small, -1.001×10^{-5} Å/°C (or $\Delta d_{005}^* = 2.365\times10^{-5}/°\mathrm{C}$), that no perceptible error would be introduced in the present experiment where the crystal was held at 15 ± 0.1°C by a thermostat. The x rays issued from line focus, the width of which was measured to be 0.22 mm. The beam-limiting slit with a circular aperture of diameter 0.3 mm was separated 298 mm from the x-ray source and 10 mm from the crystal. Then the incident

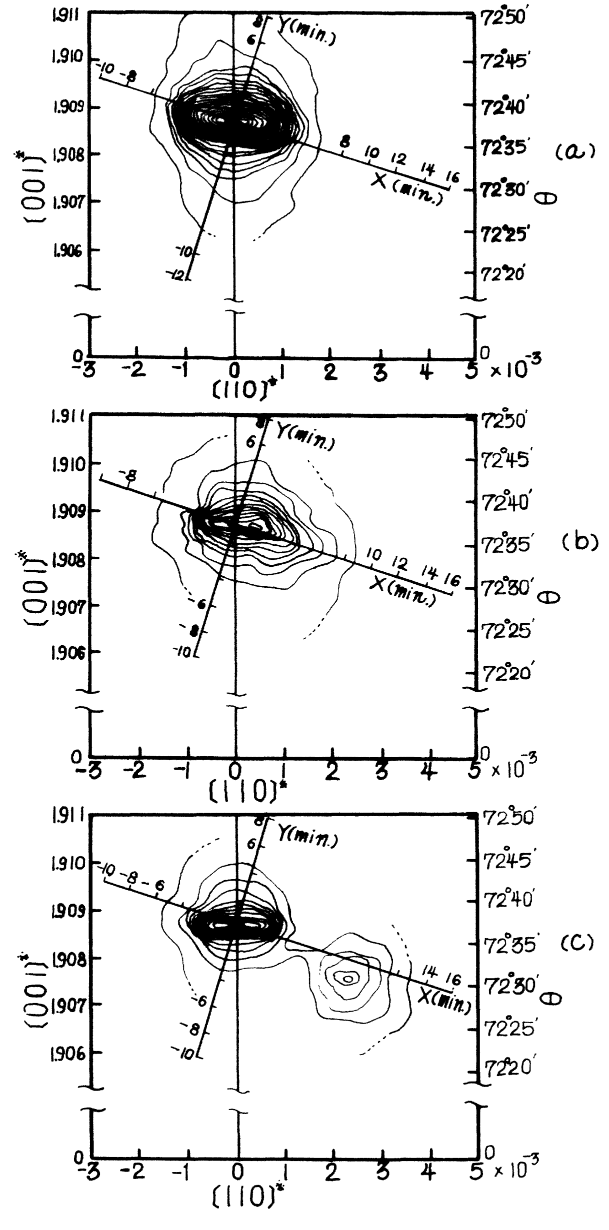

FIG. 3. Two-dimensional intensity distributions corresponding to 005 spectrum under various conditions of applied field. *X* and *Y* axes in each figure stand for the virtual axes for the construction of the distribution as indicated in Fig. 2(b). (a) $E=0$ kV/cm, (b) $E=7$ kV/cm, (c) $E=19$ kV/cm.

beam was estimated to have a maximum angle of 6′ of horizontal divergence and 16′ of vertical divergence. Therefore the x-ray beam falls on the surface of a *c*-plate crystal of dimensions 0.32 mm wide in lateral and 0.35 mm long in vertical direction. With appropriate weight functions evaluated on the above conditions, graphical analyses were carried out to resolve the degree of broadening. The low-intensity region will be expanded along the *Y* direction mainly by the combined effect of the divergence and the inhomogeneity of the radiation, while the central region will be deformed along the *X* direction on account of the width of the irradiated surface. The intrinsic intensity distribution of this specimen was estimated to have a width at half-maximum of about 2.2′. From Fig. 3 it is very apparent that on account of the aftereffects of domain motion by increasing fields, the intensity distribution 005 is deformed in the first place along the [110]* direction and split into two parts ultimately as was expected; one corresponds to the original structure, the other to a lower symmetry structure. The original maximum undergoes no change in its position, whereas the split maximum is no longer located on the original [001]* axis but displaced from it. The shift of the split maximum from the original one is described in terms of two quantities $\Delta\beta$ and Δd_S: $\Delta\beta$ is an angle which the two maxima subtend at the origin of the $(hhl)^*$ plane, and Δd_S is the increase of the interplanar spacing. Values of $\Delta\beta$ and Δd_S under various applied fields are tabulated in Table I. An analogous phenomenon was observed for 330 reflection. The splittings of the reflections in these ways might have to be interpreted as that the lower symmetry structure is pseudomonoclinic. However, the reasons why two split maxima do not appear in the present case must be clarified. They are given as follows. According to our microscopic observation of the specimen, domains started from defective spots on the electroded surface such as scratches or pits, and moreover the region relevant to the x-ray diffraction was rather small as mentioned above,

Table I. Values of $\Delta\beta$ and Δd_S under various applied electric fields.

E (kV/cm)	d_{005} (Å)	$\Delta\beta$ (min)	Δd_S (10^{-4} Å)
0	0.80701		
10	0.80703	2.6	+3.4
12	0.80700	3.1	+3.9
14	0.80701	3.5	+4.4
16	0.80702	3.7	+4.7
18	0.80704	3.9	+5.7
20	0.80703	4.1	+6.4

so that the domain walls traversing there always proceeded in the same direction.

It is very likely that the structural change that we have found would give important effects on every process of polarization reversal in $BaTiO_3$. Here we present a bold view for the mechanism of bringing about the anomalous structure change. Generally the directions of spontaneous polarization before and after its reversal are related to each other by a symmetrical operation of rotation. However, it is agreed that the anisotropy of most ferroelectrics is so high that the rotation of the polarization vector within the wall will not occur. In the case of room-temperature structure of $BaTiO_3$, e.g., $c/a = 1.01$, the anisotropy does not seem so high that the possibility of rotation of dipoles in a crystalline medium should be absolutely excluded, but it is rather realistic to assume that the rotation mechanism contributes in part to the polarization reversal. If any, the crystalline portions relevant to polarization reversal would be subjected to pure shear stress X_5 or its equivalents, because rotation of polarization takes place in an anisotropic medium. Then the polarization P_1 directed normal to the existing polarization P_3 will be developed as a result of piezoelectric coupling through a torsion modulus d_{15} or d_{24}, e.g.,[3]

$$P_1 = d_{15}X_5.$$

This will be naturally accompanied by the pseudomonoclinic deformation of the crystalline portions. It is noted that the proposed mechanism is concerned with dynamical process of domain switching. It seems to explain qualitatively all optical characters mentioned before. Especially it is of particular interest that the origin of the character (4) is understandable if we relate one direction of domain movement with right-handed rotation and necessarily the reversed direction with left-handed one.

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TWO-QUANTUM ABSORPTION SPECTRUM OF KI[†]

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We have measured the two-quantum absorption spectrum of crystalline KI in the vicinity of the fundamental absorption edge. Two-quantum absorption is a nonlinear phenomenon in which two quanta are simultaneously absorbed in an electronic transition, energy being conserved only between the electronic system and the two quanta. The electronic system is transparent to either quantum alone. Such a process has been observed by Kaiser and Garrett[1] and others, and theoretically investigated by Kleinman[2] and Braunstein.[3] In previous experiments, the absorbed quanta have both been obtained from a narrow-band laser source.

In this experiment, a continuous source of ultraviolet light has been used, allowing a broad spectrum to be investigated. To our knowledge, this is the first experimental demonstration of the utility of this technique in the range of optical energies.

The two-quantum absorption spectrum should contain as much information about a system (e.g., a solid) as does the ordinary one-quantum spectrum. Because the selection rules are very different (even-parity transitions for two-photon absorption versus odd-parity transitions for one-photon absorption), the two methods of investigation are complementary rather than identical.

The fundamental absorption edge of crystalline KI has not been well understood. Different theoretical models[4] predict similar one-photon absorption spectrum singularities, but quite different two-quantum spectra. This experiment was designed to provide a basis for choice among the various theories, and to allow the experimental study of the absorption process in bulk

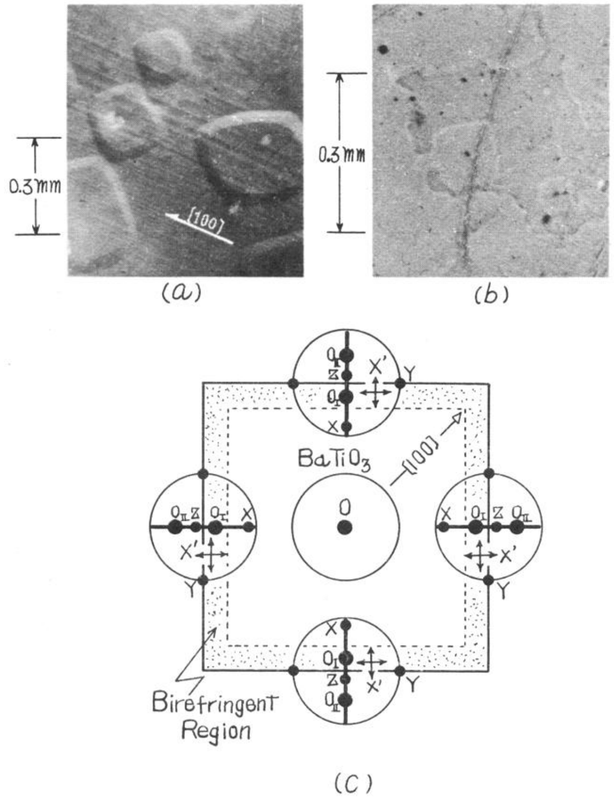

FIG. 1. Antiparallel domains in $BaTiO_3$. (a) Photomicrograph of antiparallel domains having clear dark and light contrast portions (*B* zones) as viewed with obliquely incident light; (b) antiparallel domains having uniformly dim contrast portions near the boundaries as viewed with normally incident light; (c) stereographic representation on (001) concerning the optical orientation of an approximately square domain (exaggerated): *O* denotes a unique optic axis of the tetragonal structure, O_I and O_{II} biaxial optic axes of the lower symmetry one. X' indicates the trace of the vibration plane of the fast component.